Are the Bader Laplacian and the Bohm Quantum Potential Equivalent?

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ABSTRACT

The de Broglie-Bohm ontological interpretation of quantum theory[1, 2] clarifies the understanding of many otherwise counter-intuitive quantum mechanical phenomena. We report here on an application of Bohm's quantum potential to the bonding and reactivity of small molecules. In the field of quantum chemistry, Bader has shown[3] that the topology of the Laplacian of the electronic charge density characterizes many features of molecular structure and reactivity. Examination of high accuracy *ab-initio* solutions for several small molecules suggests that the Laplacian of Bader and the quantum potential of Bohm are structurally equivalent. It is possible that Bohmian mechanics using the quantum potential can make quantum chemistry as clear as it makes non-relativistic quantum mechanics.

A set of *ab-initio* computational experiments were performed simulating H_2O, H_2O_2, and C_2H_4 to obtain the Laplacian of the electronic charge density ($\nabla^2\rho$). Bader has shown[3] that $\nabla^2\rho$ localizes lone pairs, bonded charge concentrations and regions subject to electrophilic or nucleophilic attack. $\nabla^2\rho$ acts as an objective *electron localization function*[4, 5, 6, 7], and is free from the difficulties encountered when analyzing a wavefunction by decomposition into a particular orbital basis.

In order to explore the application of the de Broglie–Bohm interpretation of quantum mechanics[1, 2] to molecular physics, we also calculated the Bohm quantum potential Q for the same molecules. Visual comparison of the three dimensional structure of these two fields (Q and $\nabla^2\rho$) strongly suggests they are equivalent.

Density functional theory calculations were carried out for the optimized ground state equilibrium geometries of water, hydrogen peroxide, and ethylene using Gaussian 94[8] at the B3LYP/6-311++G(2d,2p) level of theory[9]. Isosurfaces of the Laplacian of the electronic charge density, $\nabla^2\rho = C$, were visualized[10] for these molecules over a range of values of C and are shown in figures 1-4 for the case of water[11].

Following the analysis of Bader[3], regions of $\nabla^2\rho < 0$ correspond to electronic charge concentration, and conversely regions of $\nabla^2\rho > 0$ correspond to regions of charge depletion. The four views of H_2O shown in Figure 1 correspond to a very negative value of $\nabla^2\rho$. The electronic charge concentrations associated with the nuclei as well as the two lone pair charge concentrations on the oxygen atom are visible. For a less negative value of the Laplacian (figure 2), concentrations of electronic charge on the OH bonds become visible. At $\nabla^2\rho = 0$ (figure 3) the outline of the entire molecule emerges. Finally, for a positive value of $\nabla^2\rho$ (figure 4), three regions of valence charge depletion are visible, as well as the region of depletion surrounding the Oxygen's core electrons.

The structure of $\nabla^2\rho$ may be formally defined in terms of the attractors, repellors, and saddle points in $\nabla\nabla^2\rho$ and their interconnections[3]. In the case of water, there is one attractor at each nucleus, one in each lone pair region, one on each bond, and

no others (figures 1-3).

To compute Bohm's quantum potential[1] we first express the wavefunction in polar form, $\Psi = Re^{iS/\hbar}$. The quantum potential for an N electron molecule using the Born-Oppenheimer approximation is then:

$$Q = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\frac{\nabla_i^2 R}{R}.$$

Q is a function of the $3N$ coordinates of all of the electrons, and ∇Q is, in Bohm's interpretation of quantum mechanics, the nonlocal quantum force that acts in addition to the classical forces on each electron.

For a one-electron molecule, Q reduces to

$$Q_1 = -\frac{\hbar^2}{2m_e}\frac{\nabla^2\sqrt{\rho}}{\sqrt{\rho}}.$$

Visualization in three-dimensional physical space of the $3N$ dimensional quantum potential for multiple electron molecules was accomplished by calculating $\overline{Q}$ as a function of $\Psi_1 = \sqrt{\rho/N}$ where Ψ_1 is the solution of the exact one-electron Schrödinger equation for an N-electron molecule[12]. In this case, $\overline{Q}$ is identical to Q_1 times a constant. In terms of the charge density (ρ) and the Bader Laplacian ($\nabla^2\rho$),

$$\overline{Q} = \nabla^2\rho/2\rho - (\nabla\rho/2\rho)^2.$$

Isosurfaces of the (one electron) Bohm quantum potential for H_2O are shown in figures 5-8 for a range of values. The topology of this field (the structure of its foliation by isosurfaces, or, equivalently, the attractor, repellor, and saddle connections of its gradient) appears identical to that of $\nabla^2\rho$ in the case of water, as well as in the cases of all other molecules examined by the authors.

There are some geometrical differences between the two fields. The presence of the factor $\rho^{-1/2}$ in the expression for $\overline{Q}$ implies that the magnitude of $\overline{Q}$ may be large

far from the nuclei. In Bohm's picture, this factor accounts for nonlocality (distance independence) in quantum mechanics. In the molecules we examined, this factor accounts for structures in $\overline{Q}$ extending over larger distances than those in $\nabla^2\rho$. It may also be that the quantum force ∇Q acting on the electrons is responsible, in part, for the "concentration" of electronic charge (i.e. regions of Bader Laplacian < 0) in bonding and lone pair locations.

While other authors have compared the structure of $\nabla^2\rho$ with $\nabla^2\sqrt{\rho}/\sqrt{\rho}$ for atoms[13] and molecules[14], this is the first time it has been done in three dimensions, and to our knowledge the first time that a connection of the Bader chemical theory to the de Broglie–Bohm quantum potential has been made.

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[11] Supplementary data available on the world wide web at http://www.nas.nasa.gov/∼creon/nano/quantum-potential/

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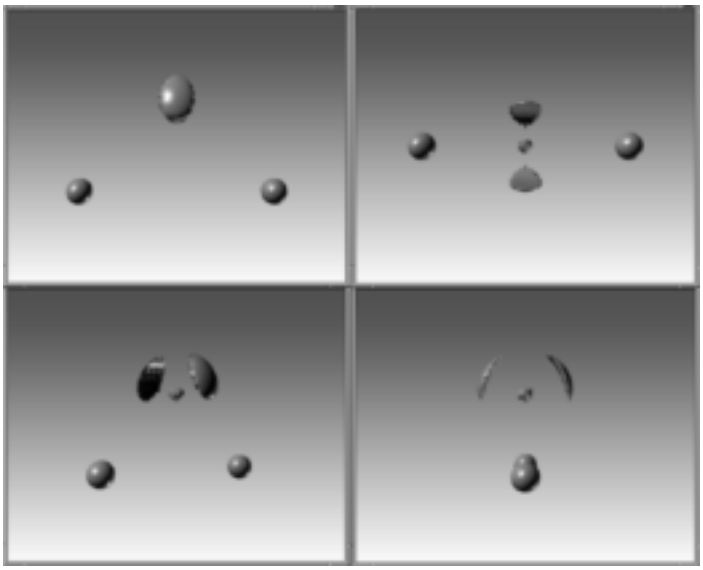
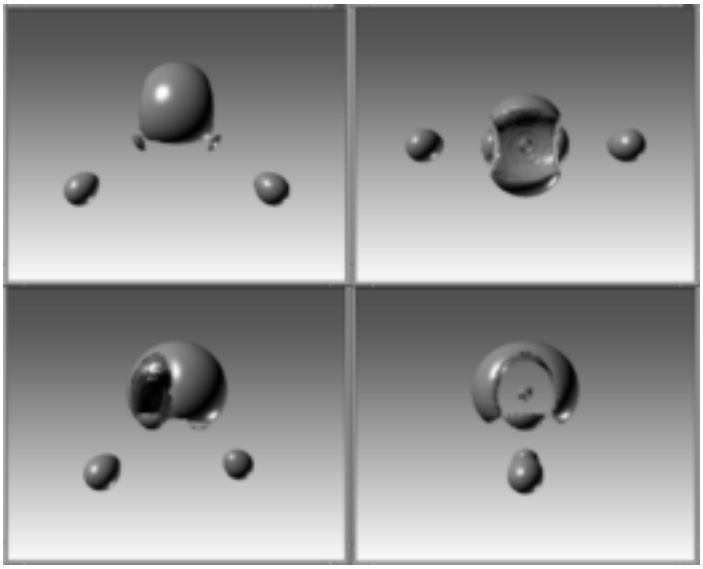


figure 1



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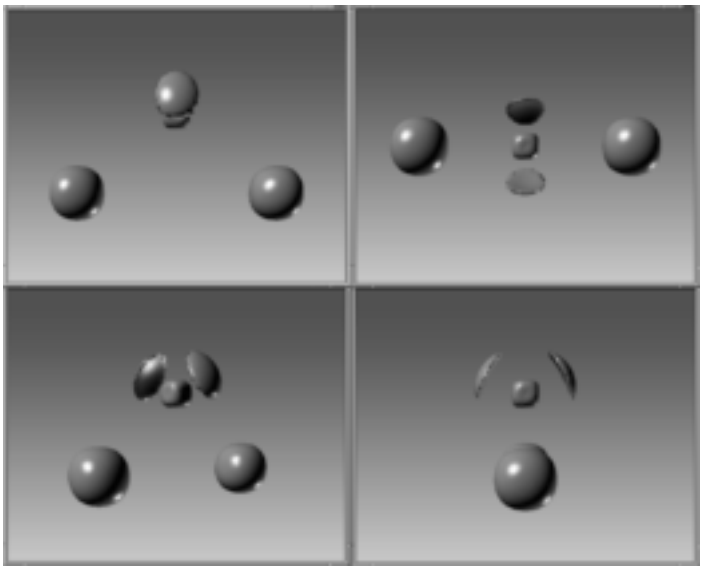

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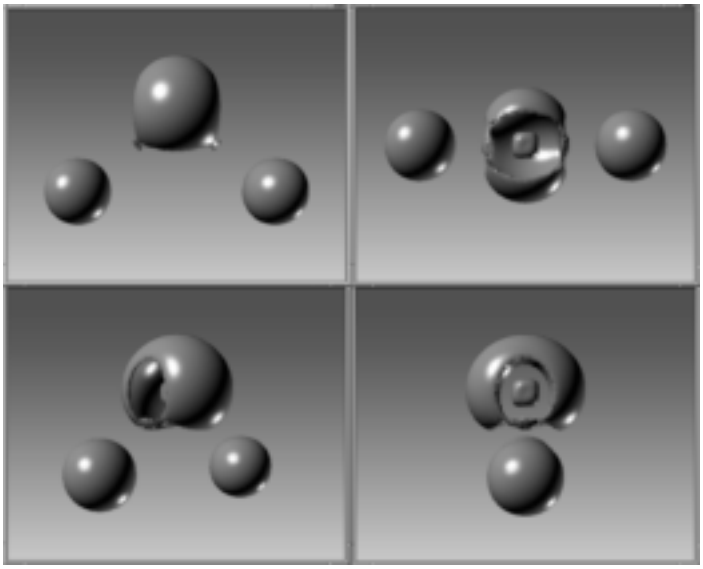

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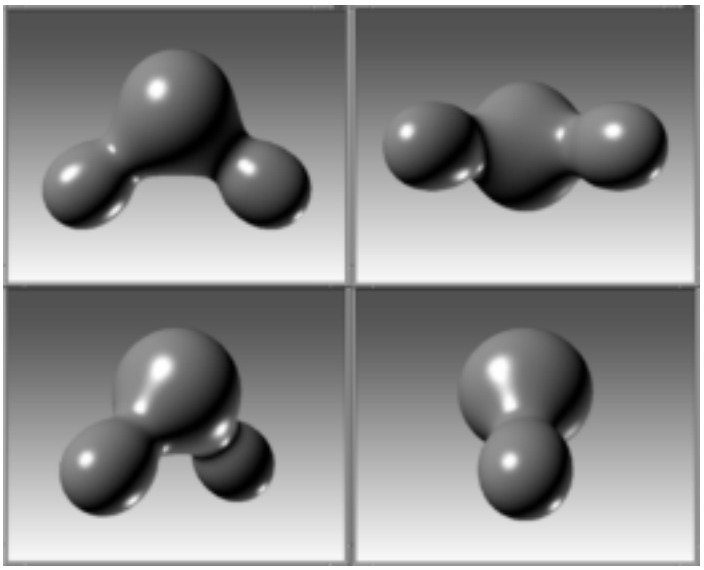

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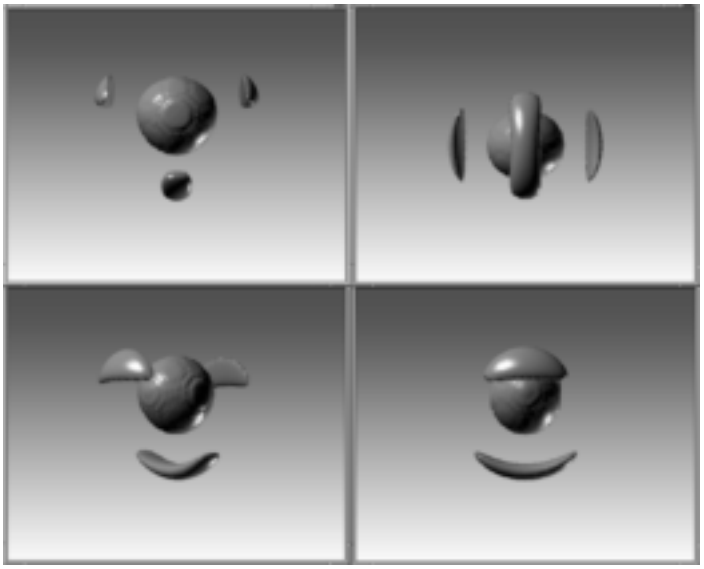

figure 4

figures 1-4: Each figure shows four views of an isoscalar surface of the Laplacian of the charge density for H_2O. Figure 1 ($\nabla^2\rho \ll 0$) shows local minima at the nuclei and at the locations of the oxygen lone pairs. Figure 2 ($\nabla^2\rho < 0$) shows additional local minima on the bonds. In figure 3 ($\nabla^2\rho = 0$) the outline of the entire molecule is visible. Figure 4 ($\nabla^2\rho > 0$) shows regions of valence charge depletion.

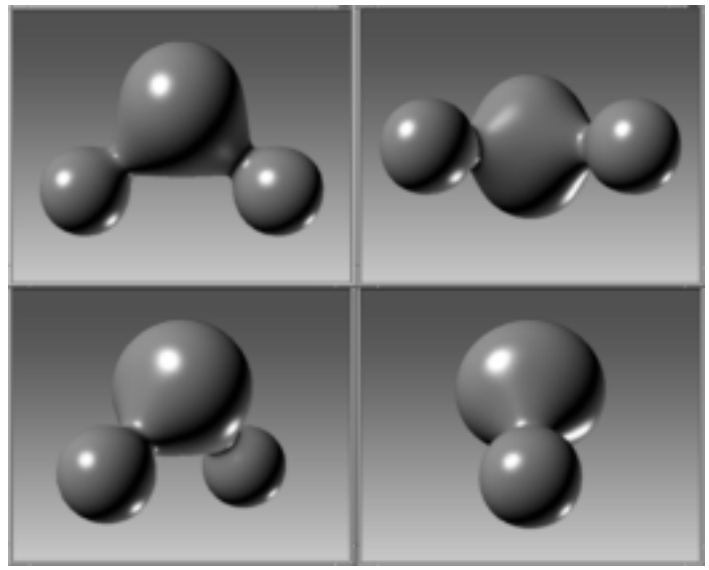

figure 7

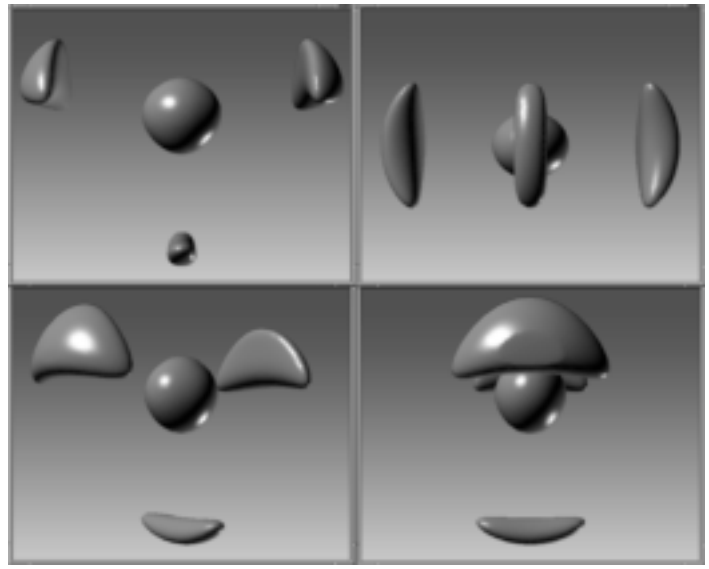

figure 8

Figures 5-8: Each figure shows four views of an isoscalar surface of the (one electron) Bohm quantum potential for H_2O. The topology and symmetry are identical to the Bader Laplacian ($\nabla^2\rho$, figs. 1-4) for H_2O and other molecules.

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